Synthesis and Characterization of Nafion-SiO_2 Composite Membranes as an Electrolyte for Medium Temperature and Low Relative Humidity

Mahreni[1)], Eniya Listiani Dewi[2)], Tjukup Marnoto[1)], Harso Pawignyo[1)], Purwo Subagyo[1)], Endang Sulistyowati[1)]
[1)]*Department of Chemical Engineering, Faculty of Industrial Technology*
Universitas Pembangunan Nasional "Veteran" Yogyakarta.
Jl. Lingkar Utara 104 Condong Catur Yogyakarta Indonesia (55283)
Telp: 0274 486889
[2)]*Badan Pengkajian Penelitian dan Teknologi*
Jl. M.H. Thamrin 8 Jakarta (10340)
Email: mahreni_03@yahoo.com

***Abstract* - The weakness of the Nafion membrane as electrolyte of PEMFC associated with physical properties that is easy to shrink at temperatures above 80°C due to dehydration. Shrinkage will decrease the conductivity and membrane damage. Nafion-SiO_2 composite membranes can improve membrane stability. The role of SiO_2 in the Nafion clusters is as water absorbent cause the membrane remains wet at high temperatures and low humidity and conductivity remains high. The results showed the content of 2.8 wt% of SiO_2 in the Nafion membrane, the conductivity of composite membrane is higher than the pure Nafion membrane that are 0.127 S cm^{-1} in dry conditions and 0.778 S cm^{-1} in wet conditions at room temperature. Compared with the pure Nafion membrane conductivity are 0.0661 S cm^{-1} and 0.448 S cm^{-1} respectively in dry and wet conditions.**

I. INTRODUCTION

Organic-inorganic composite membranes can replace the Nafion membrane. Because the composite membranes (i) generally have a higher thermal stability compared to organic membranes, (ii) higher the degree of tortuosity [1][2]. So it can reduce permeability of hydrogen and oxygen gas and fuel efficiency will go up, (iii) the presence of hygroscopic (inorganic compound) as well as SiO_2 in the polymer network increased the number of hygroscopic functional groups and can increase the water uptake rate (WUR) [3][4]. So that the composite membranes can be used as an electrolyte in PEMFC at higher temperatures and low humidity conditions. The advantages of the PEMFC that operated at high temperatures and low relative humidity can increase the resistance of the electrode (Pt) of CO poison and can eliminate humidifier device. In this study, composite membranes synthesized by using a Nafion solution and TEOS through hydrolysis and condensation reactions (sol-gel reaction). Sol-gel method was chosen because it has been shown to be able to easily produce nanostructure composites [5][6].

Problems in synthesis of Nafion-SiO_2 composite membranes is the separation of organic and inorganic phase so that the resulting membrane has a structure that is not homogeneous and the particle size of the membrane. Inorganic particles (SiO_2) in the organic phase which has been generated from previous studies still in micro size. So can not enter into the Nafion clusters [7][8][Chris Yang et al, 2004]. The presence of SiO_2 in the Nafion clusters that have a diameter of 4-10 nm is essential to be a bridge of proton hopping from one cluster to another cluster and increase proton transfer rate. Sol- gel process allows producing nanometer-scale of SiO_2 due to the mixing of the two organic-inorganic materials carried in the same phase (solution phase). So that the interaction between the two component occurs at the molecular level. Targets to be achieved is to produce a composite Nafion-SiO_2 membrane that the particle of SiO_2 having a size smaller than the size of the Nafion clusters. In this study, composite membranes synthesized by using a Nafion solution and TEOS through hydrolysis and condensation reactions (sol-gel reaction) in the two kind of solvent thud are polar protic and polar aprotic solvent [9].

This research aims to produce a Nafion-SiO_2 nanocomposite membranes with high proton conductivity at low relative humidity by studying the influence of inorganic content in the organic phase to the physical-chemical and electrochemical properties of the resulting composite membranes. Analysis of chemical-physics properties of the membrane covering (i) the morphology, distribution and element composition of the particles using SEM-EDS. Analysis of the electrochemical properties analyzed using EIS and water absorption levels (water uptake rate) analyzed using gravimetric method. The degree of transparency of the composite was analyzed using UV-Vis spectroscopy [10][11].

II. EXPERIMENT AND METHOD

The materials used to produce a composite Nafion -SO_2 membranes: include (i) 5 wt% Nafion solution in isopropanol (IPA) solvent (Du Pont), (ii) tetraethoxyorthosilicate solution (TEOS) 98% by weight (Merck), (iii) dymethyl formamide (DMF) (Merck), (iv) 98 wt% sulfuric acid and (v) peroxide 37% by weight. All of the material used without pretreatment. The equipment consists of: (i) ultrasonic stirrer, (ii) a Petri dish, and (iii) atmospheric oven.

20 g of 5 wt% Nafion solution was evaporated in a fume hood until the weight to 1 gram. After evaporated Nafion turned into solids. Nafion solids redissolved in DMF solvent to a solution of 5 wt% Nafion in DMF solvent. To produce a homogeneous solution, a mixture of solid Nafion and DMF was stirred using an ultrasonic stirrer for 2 hours. After that,

TEOS was added to the mixture of Nafion-DMF and continue to stir for 6 hours.

The content of SiO_2 in the Nafion varied by varying the ratio of TEOS/Nafion in the range of: 0; 0.05; 0.1; 0:15; 0:20; 0.25; 0.30 (w/w). To release the trapped air bubbles, the solution was allowed to stand without stirring for 24 hours. The solution was then heated in an oven at a temperature of 90° C for 2 hours to evaporate the solvent, then continued heated at 110° C for 4 hours to evaporate the volatile molecules. Composite membrane which can be later removed from the Petri dish and washed with 0.5 M sulfuric acid solution for 1 hour at 80°C and washed in a solution of peroxide 3 wt% for 1 hour at the same temperature. To eliminate the peroxide and sulphate which remains on the surface of the membrane, the membrane was washed in the distilled water at 100°C until the washing water is neutral. Membrane was dried at 60°C and left for 24 hours in the room condition before characterized. A description of the experiment shown in Fig.1.

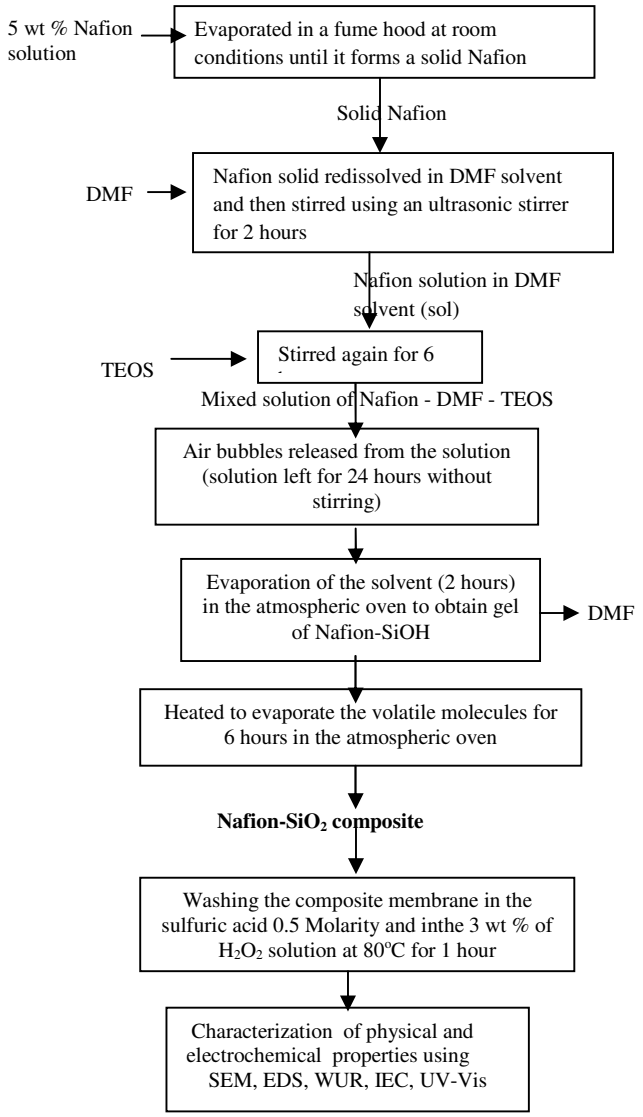


Figure 1. Flow chart of synthesis of Nafion-SiO_2 composite membranes using sol-gel method

To study the effect of solvent type on the properties of the resulting composite membrane, then the next step is synthesis of composite membranes using IPA solvent. Nafion solution was not evaporated but directly mixed with TEOS and were treated the same as the first step.

Characterization of morphology is crucial to the composite membranes to determine the distribution of inorganic particles and the microstructure of the membrane [12]. Analyses were performed using SEM (JEOL JSM 6510 LA) (scanning electrone mycroscope) with magnification 1000 times. Element analysis can provide information about the composition of elements present in the resulting composite membrane. Analyses were performed by means of EDS performed after morphological analysis with the same instrument (JEOL JSM 6510 LA).

Water absorption rate (water uptake rate, WUR) were analyzed using gravimetric methods. Calculated based on the difference in wet weight (W_{wet}) minus dry weight divided by dry weight (W_{dry}). Wet membrane is a membrane after immersion in aquadest for 48 hours. Dry membrane is a membrane after drying in an oven at a temperature of 100°C for 8 hours. Water absorption rate can be calculated using the following equation [2]

$$Wup = \frac{W_{wet} - W_{dry}}{W_{dry}} x100\% \quad (1)$$

III. RESULT AND DISCUSSION

3.1 The results of direct observation.

We produced 14 composite membranes. Seven composite membranes produced using DMF solvent with a ratio of TEOS/Nafion in the range of (0; 0.05; 0.1; 0:15; 0.2; 0:25 and 0:30) (w / w) respectively referred to as A1: B1: C1: D1: E1; F1 and G1. Seven other membrane generated using IPA solvent is referred to as A2: B2: C2: D2: E2: F2 and G2.

Table 1. Nafion-SiO_2 composite membranes using DMF solvent) and the ratio of R (TEOS / Nafion) was varied from (5/100-35/100) (w/w), evaporation temperature 90°C and annealing temperature 120°C, for 6 hours. Diameter of the membrane is 10 cm and the thickness is 70±5 µm.

No.	Code	Appearence	Ratio TEOS/Nafion (w/w)
1	A (1)	Transparent, homogeneous, no cracks, not brittle.	0
2	B(1)	Transparent, homogeneous, no cracks, not brittle.	5/100
3	C(1)	Transparent, homogeneous, no cracks, not brittle.	10/100
4	D(1)	Transparent, homogeneous, no cracks, not brittle.	15/100
5	E(1)	Transparent, homogeneous, no cracks, not brittle.	20/100
6	F(1)	Transparent, homogeneous, no cracks, not brittle.	25/100
7	G(1)	Transparent, homogeneous, no cracks, not brittle.	30/100

Table 2. Nafion-SiO 2 composite membranes using IPA solvent and R is varied (5/100-30/100) (w / w), evaporation temperature (90 ° C) , annealing temperature at120°C for 6 hours. Diameter of the membrane 10 cm and thickness 70±5 µm.

No.	Code	Appearence (colour)	Ratio TEOS/Nafion (w/w)
1	A (2)	Transparent, homogeneous, no cracks, not brittle.	0
2	B(2)	Transparent, homogeneous, no cracks, not brittle.	5/100
3	C(2)	Transparent, homogeneous, no cracks, not brittle.	10/100
4	D(2)	Transparent, homogeneous, no cracks, not brittle.	15/100
5	E(2)	Transparent, homogeneous, no cracks, not brittle.	20/100
6	F(2)	**Partially transparent**, heterogeneous, no cracks, not brittle.	25/100
7	G(2)	**Partially transparent, heterogeneous**, no cracks, brittle.	30/100

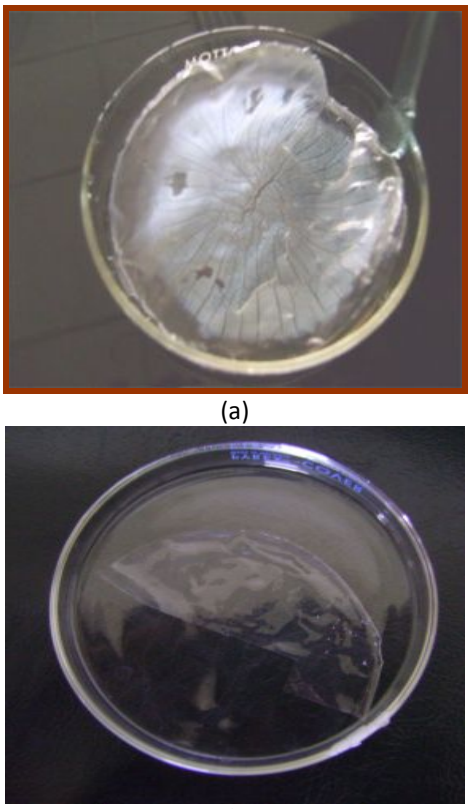
From Table 1 and 2 it can be concluded that all membranes produced using DMF solvent are all transparent, homogeneous, not broken and not brittle. While the membrane with IPA solvent are not all transparent. Samples of F2 and G2 showed partially transparent. From the results of direct observations can be concluded that phase separation occurs on F2 and G2 sample.

The reason why the membrane phase separation occurs in the resulting composite membrane by using a polar protic solvents such as IPA. Because Isoprophylalcohol releasing OH^- ions in the solution. Dymethylformamide also polar but aprotic solvents. This means that in solution. DMF does not release OH-ions. The effect of OH ions is as a competitor with the SiOH groups to bind to the SO_3H^+ of Nafion molecules allowing some SiOH are not bonded with Nafion and caused the separation of organic-inorganic phase. This phase separation can be observed as shown in Figure 3 (b).

Figure 3 shows the differences between the composite membrane using aprotik solvent (a) and protic solvent (b). Based on research conducted by [13] there are the relationship between the chemical interaction and the phase separation. It was proved also by the same reverence there is a relationship between % Transmittance of UV-Vis light and the degree of transparency of the composite membrane, The higher the % transmittance higher degree of transparency. It means the smaller particle size of the constituent. Smaller the particle size higher ability of the composite to transmit UV light so higher % transmittance. The results of the analysis using a UV-Vis light spectroscopy is shown in Table 3.

Way of testing the resulting membranes using UV-Vis spectroscopy is cut the membrane to the size of 2x2 cm and then cleaned with soft tissue and then scanned by using a UV-Vis in the range of wavelength of 190 nm to 1100 nm. The wavelength is divided into three regions namely wavelength near infrared (760-1100) nm, Visible (380-780) nm and UV (190-380) nm.

Table 4 shows all of the resulting composite membrane transmittance in the wavelength region of (190-1100 nm), Could be seen that the transmitancy of all of the membrane higher then 82 %.



(a)

(b)

Fig. 3. The appearance of the composite membranes: F1 (a), F2 (b).

Table. 3. % Transmittance of the composite membrane.

No.	Code	Range of the Transmittance (%T)			
		Near infra red =780-1100 nm	Visible = 380-780 nm.	Ultra Violet =190-380nm	Total =190-1100 nm.
1	A1	94.81 %	94.25 %	85.12 %	92.54 %
2	B1	90.94 %	89.42 %	80.30 %	88.05 %
3	C1	94.53 %	93.70 %	86.04 %	92.39 %
4	D1	93.62 %	92.27 %	83.66 %	90.95 %
5	E1	93.68 %	92.03 %	78.14 %	89.71 %
6	F1	93.60 %	92.08 %	79.62 %	90.01 %
7	G1	91.68 %	87.40 %	55.23 %	82.19 %

Based on the results of theoretical calculations and prove by using TEM measurements of other composite membranes in [13] it can be concluded that if the % transmitance higher then 82% indicates the composite membrane have the particle diameter below 100 nm. The results of this study shows, all of the composite membranes that produced by using DMF solvent has transparent appearance. So could be concluded that: (1) in the composit membrane there has been a chemical interaction between Nafion and SiOH functional groups and (ii) SiO_2 particle diameter below 100 nm. This allows the SiO_2 particles can get into the Nafion clusters.

As has been described in recent literature [14] that the proton transfer in Nafion membrane depending on the moisture content because in the membrane. The proton (H^+) can move if it binds with water molecules in the form of hydronium ion (H3O +). The presence of SiO_2 in the Nafion clusters can increase the amount of mlecule water. The more

molecule water in the Nafion clusters, make the proton transfer from one cluster to the next cluster increases.

3.2 The results of SEM-EDS analysis.

Morphology of Nafion-SiO_2 composite membrane shown in Figure 2. The sample A1 is pure Nafion, B1 is the composite membrane with R = 0.05; C1 (R = 0.1) and F1 (R = 0.25). From this figure, known that the structure of the cross sectional of membrane surface is homogeneous and no phase separation between organic-inorganic phase.

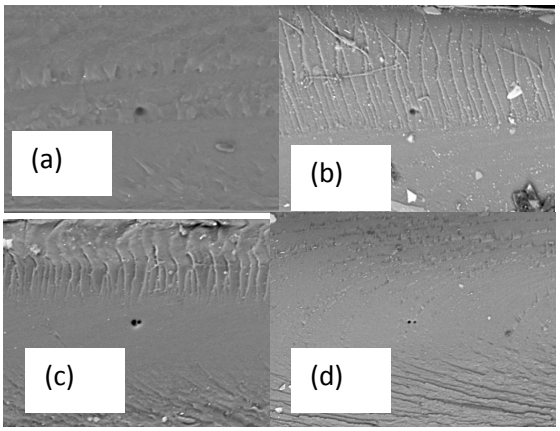


Fig. 2. Mophology of the: (a) pure Nafion, (b) the composite with the R = 0.05 (w/w), (c) R = 0.1 (w/w) and (d) R = 0.25 (w/w).

Elemental analysis to the composite membrane performed to determine the composition of the component quantitatively. It is important to prove that the inorganic components are incorporated into the polymer matrix of Nafion and not eroded when the membrane was washed with sulfuric acid, peroxide and aquades. The results is shown in Table 4.and Fig 3.

TABLE 4. ATOMIC % OF THE COMPONENT IN THE COMPOSITE MEMBRANES.

		Atomic %			
No.	Element	N112 (A1)	B1	C1	F1
1	C	31.37	42.48	48.4	43.74
2	O	6.77	11.44	14.21	10.51
3	F	59.98	45.22	35.86	44.67
4	S	1.88	0.65	1.11	0.79
5	Si	-	0.2	0.42	0.29
Total		100 %	100 %	100 %	100 %

From this analysis known that the pure Nafion consists of the elements C, O, F and S and element in the composite membrane beside thus component there is silicate as additive component.

Silicate in the polymer matrix increases with R value. Proves that the silicata is not eroded after the membrane was washed. The content of silicate in the sample B1 (R = 0.05) was 0.2% and in the C1 (R = 0.1) is 0:42%. But in F1 (R = 0.25) decreased to 0.29% atom due to the larger R the greater the diameter of the silicate particles. This causes the particles of silica are beyond the cluster and eroded when the membrane was washed so decreased of silica content. This is consistent with the results of UV analysis indicated if r value increase the % Transmittance getting smaller.

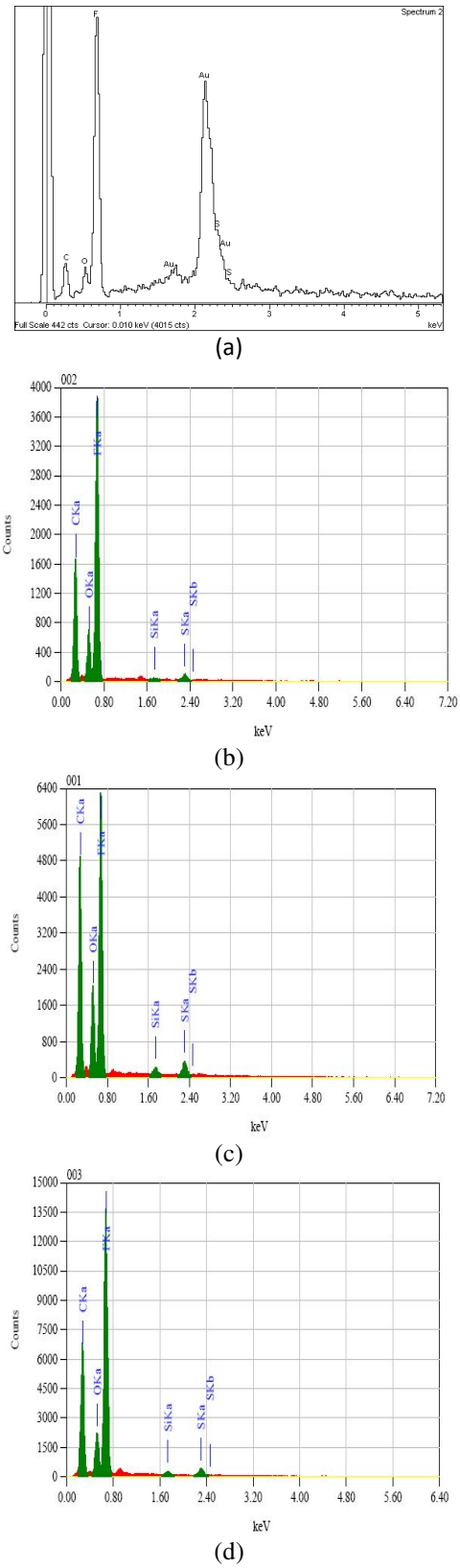


Fig. 3 The EDS pattern of the composite membrane: (a) A1 (pure afion), (b) B1 (R = 0.05 w/w), (c) C1 (R = 0.1 w/w) and (d) F1 (R = 0.05 w/w).

3.3 Electrochemical characterization.

Conductivity (σ) measured from the measurements of resistance (R) using the relation σ = l / (AxR) where A is the surface area in contact with the probe and l is the thickness of the membrane. R value is measured using AC impedance (EIS) (model SA1125B, Solartron Co.). Conductivity was calculated by the equation σ = 1 / R [2] [15].

Table 5. shows the conductivity of the composite membranes that produced by the DMF solvent . Analyses were conducted on the dry and wet condition. The purpose test in dry conditions is to ensure whether the Nafion-SiO_2 composite membrane produced can be used as an electrolyte in the PEMFC at low humidity conditions.

TABLE. 5. CONDUCTIVITY OF THE COMPOSITE MEMBRANES IN DRY AND WET CONDITION.

No	Ratio of TEOS/ Nafion (w/w)	Ratio of SiO_2/Nafion (w/w)	Code	Conductivity (S cm^{-1}) Dry membrane	Wet membrane
1	0	0	A1	0,0661	0,448
2	5	0,01442	B1	0,0247	1,47
3	10	0,02884	C1	0,127	0,778
4	15	0,04326	D1	0,0518	0,553
5	20	0,05768	E1	0,0280	0,242
6	25	0,07210	F1	0,0186	0,187
7	30	0,08665	G1	0,00855	0,080

Table 5 shows that the sample C1 is the best composite membrane a sign by the conductivity of the membrane at dry condition that is 0127 S cm^{-1} and the wet membrane conductivity is 0778 S cm^{-1}. Compared with the pure Nafion membrane conductivity is 0.0661 and 0448 respectively on dry and wet conditions. Table 5 also shows that the addition of silica above the value R = 0.1 can not raise the conductivity significantly and the value R = 0.2 to 0.3 decreased the conductivity (smaller than the conductivity of pure Nafion). This is because the greater the R value, the greater the particle size so that the particles can not enter into the Nafion clusters and eroded when the membrane was washed in a sulfuric acid and peroxide solution.

Table 6. Show WUR of composite membranes was measured at 80°C temperatures. If the R value increase, WUR increase due to the more silicate in the Nafion matrix. The relationship between conductivity and WUR in this study can not be compared because of different measurement temperatures.

Based on the analysis of UV, and the EIS indicates that the value of R> 0.1, resulting the composite membrane which the SiO_2 particle size larger than the size of Nafion cluster so that the SiO_2 particles outside the Nafion cluster. Particles that located in outside the Nafion clusters can not as the bridge of proton hopping so it can not raise the conductivity.

TABLE 6. WATER UPTAKE RATE OF THE COMPOSITE MEMBRANES

No.	Ratio of TEO/Nafion	Code	% WUR
1	0	A1	19.01
2	0.05	B1	20,45
3	0.1	C1	21,3
4	0.15	D1	26,41
5	0.2	E1	27,65
6	0.25	F1	37,12

IV. CONCLUSSION

From the results of direct observations, the membrane produced using DMF solvent is transparent indicating that the structure of the resulting composite membrane is the nanocomposite. Membranes produced using IPA solvent there are two types of sample F (2) and G (2) has a heterogeneous structure (partially transparent) indicates that the phase separation between the organic components (Nafion) and inorganic component (silicate). This is because Isoprophylalcohol (IPA) is a polar protic solvent. Polar protic solvent produces OH ions in solution. Ion hydroxil will be a competitor for the SiOH ion. Hydroxyl ions will bind to the sulfonate group and prevents bonding between the sulfonate and SiOH. Blocking by OH ions to the sulfonate group causes phase separation and heterogeneous structure of the membranes as well as for F2 and G2 sample. The results of the EIS analysis show that the conductivity of the sample C1 is the best composite membrane. C1 is a composite membrane samples produced using DMF solvent with a value of R = 0.1 has the highest conductivity in both dry and wet conditions is 0127 S/cm (dry) and 0778 S/cm in wet conditions.

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